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The Photo-electric Fatigue of Zinc.

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Hertz's observation* that ultra-violet light can facilitate the passage of an electric spark led to the discovery of other photo-electric actions.† In the earliest experiments on the photo-electric effect of metals it was noticed that the action was diminished by exposure to light. Thus Hallwachs,‡ who found that a metal becomes positively electrified under the influence of ultra-violet light, states that "old surfaces no longer show the phenomenon. The radiation itself lowers the potential to which the plates can be electrified, so that with any succeeding experiment made with the same surface the potential obtained is lower, while the rise to it takes place more rapidly, and the decrease is greater than when for the same interval of time between the experiments the plate was not illuminated."

This diminution of the photo-electric action is spoken of as the "fatigue" of metals under the influence of light. It has received attention from many physicists, of whom Buisson§ and Ladenburg‖ may be specially referred to.

The present paper deals with the manner in which the photo-electric activity of zinc diminishes when the metal is exposed to light.

Description of Apparatus.

1. *Source of Light.*—Some preliminary experiments were made with the electric arc, limelight, and burning magnesium, but these proved too unsteady to give reliable results over long intervals of time, though the general character of the fatigue curves was similar to that of the curves obtained later with a steady source. A Nernst lamp was found to give enough actinic light for the observations, and when the current was supplied from a battery of large storage cells this source remained sufficiently steady for hours. When the lamp was run on the town mains the variations in voltage

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* 'Wied. Ann.,' vol. 31, p. 983, 1887.

† See J. J. Thomson, 'Recent Researches' and 'Conduction of Electricity through Gases.'

‡ 'Phil. Mag.,' Series 5, vol. 26, p. 78, 1888.

§ 'Comptes Rendus,' vol. 130, p. 1298, 1900; 'Ann. Chim. Phys.,' vol. 24, pp. 320—398, November, 1901.

‖ 'Ann. d. Physik,' vol. 12, pp. 558—578, September, 1903.

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of the supply caused considerable fluctuations in the current through the lamp and in the intensity of the light, as shown by corresponding irregularities in the fatigue curve.

2. *The Testing Vessel and Electrometer.*—The apparatus was practically a parallel-plate air condenser enclosed in a metal box. The construction of the testing vessel employed is shown in the diagram (fig. 1). The vessel was of brass, closed at top and bottom by brass covers screwed on. The top cover had a circular aperture closed by a quartz window, B. The central electrode, A, was insulated from the base by an ebonite plug, E. Small iron cups containing mercury are shown at D_1 and D_2, the latter being in metallic connection with the case of the apparatus, which was permanently earthed. A strip of copper supported by a wooden lever served to make or break the connection between the mercury cups, whilst the observer remained at a distance from the apparatus. C is a thick lead plate with a circular hole, placed between the light and the apparatus to shield the latter from ineffective radiation.

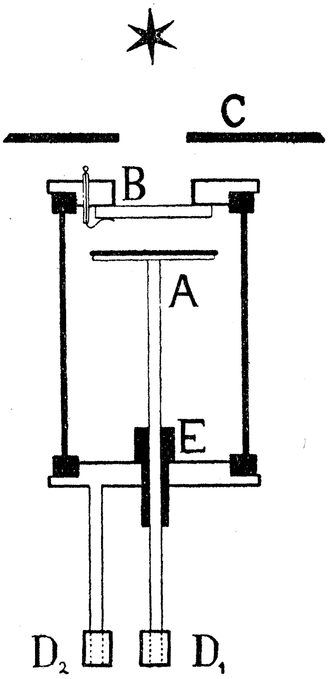

Fig. 1.

In most of these experiments the upper plate of the condenser was formed by the lower face of the quartz window, rendered conducting by phosphoric acid, as suggested by Strutt. In other experiments it consisted of a piece of wire gauze, supported by, but insulated from, the cover of the apparatus. This upper plate was connected to the positive terminal of a battery of small accumulators (200 elements), the other end of the battery being to earth. The lower plate of the condenser, formed by the piece of zinc to be tested, was connected to one set of quadrants of an electrometer, the other set being earthed. The rate of leak of electricity across the gap was measured by noting the time taken for the electrometer needle (observed with telescope and scale) to turn through a given angle. A Kelvin electrometer, with replenisher and gauge, was used most frequently, but in some experiments an electrometer of the Dolezalek type was employed.

3. *Method of Experimenting.*—The zinc plates used in these experiments were 5 cm. in diameter. They were either polished or amalgamated. In the former case the final polishing was done with rouge paper, either by hand or

in the lathe. Ladenburg* has pointed out that as the polish increases the discharge approaches a maximum, a result that was confirmed in these experiments. The surface of the amalgamated plate was renewed by rubbing a few globules of mercury over it with a cloth. The freshly polished or re-amalgamated plate was placed in the testing vessel, on the central electrode, the cover put in position, the electrical connections made and the Nernst lamp lighted. Observations were usually commenced within two minutes of the preparation of the plate and were continued as long as desired, readings of the rate of leak being generally taken at intervals of two minutes.

4. *Results of Experiments with Zinc.*—The general course of the decay curves was similar for polished and amalgamated zinc. The fatigue was very rapid immediately after exposing the metal to light, but after some time (usually 20 or 30 minutes from the commencement) the rate of decay became much slower. Such a result would be expected in the case of a change following the "compound interest law," but the initial decay observed compared with that in the later stages was even more rapid than would be required by such a change. The results are most clearly exhibited by plotting them on semi-logarithmic paper, where the ordinate represents the logarithm of the rate of leak, the abscissa the time from the first illumination of the plate. An exponential formula would be represented by a straight line. The curve representing the observed results consists of two parts, the first (AB) convex to the origin; the second (BC) a straight line inclined to the axes. That is to say, after about half an hour's exposure to light the decay of the activity may be expressed by a single exponential term. This was confirmed by continuing the observations over a long period.

The curve reproduced in fig. 2 shows that after the first rapid change the activity decays in an exponential manner for several hours.

The changes taking place during the first 100 minutes of the experiments are shown more clearly in figs. 3 and 4. The vertical scale in fig. 2 is not the same as in the later diagrams, for in these the rates of leak were about 10 times those recorded in the former figure. If the straight portion is continued backwards in the manner shown in fig. 2, and the difference between the rates of leak corresponding to P and P′ is plotted against the time on semi-logarithmic paper, another straight line is obtained, more steeply inclined to the horizontal axis. This shows that the experimental results can be represented by the sum of two exponential terms, so that the photo-electric activity is given by the empirical formula

$$I = K_1 e^{-\lambda_1 t} + K_2 e^{-\lambda_2 t}.$$

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* *Loc. cit.*

For polished zinc this formula was found to apply under varied conditions, respecting the polish of the plate and the intensity of the illumination.

The value of λ_1 was more than 10 times that of λ_2, and K_1 was of the same order of magnitude as K_2.

5. In order to render more evident the agreement between the results of observation and those obtained by calculation from the above formula, the following table has been constructed for a selected case. This series of observations (August 7, 1905) was made with well polished zinc, illuminated by a 1-ampère Nernst lamp on a 110-volt circuit. The first reading was taken three minutes after the polishing of the zinc plate was completed. The exact instant of lighting the Nernst lamp was not noted in this experiment, but it

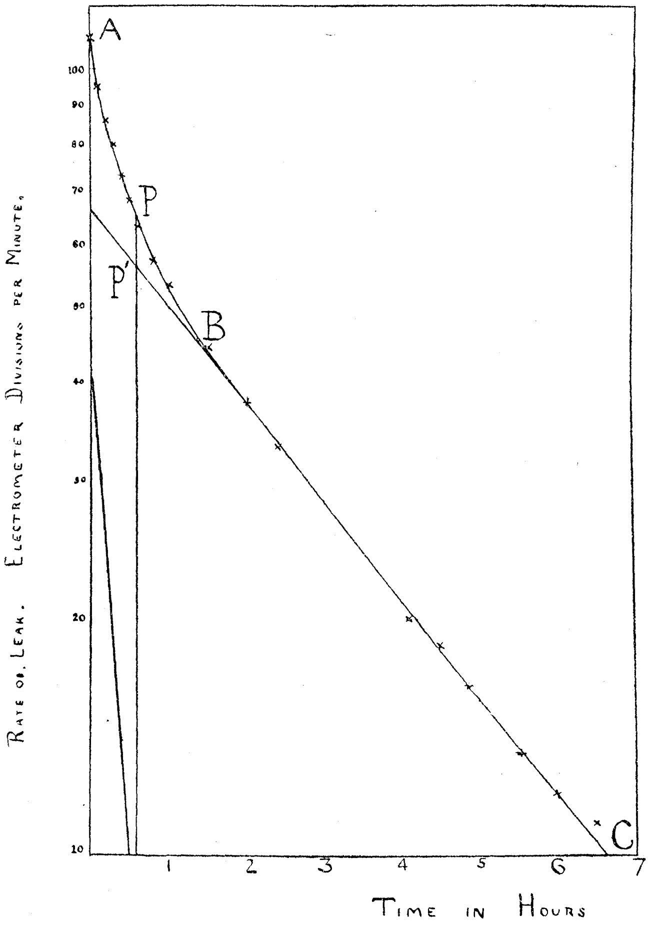

Fig. 2.

Photo-electric Fatigue of Zinc. Experiments made June 30, 1905. Nernst lamp taking 0·25 ampère on 110-volt circuit.

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is assumed to have taken place two minutes after polishing. The first column of the table gives the time in minutes from the first illumination of the plate. The last column gives the observed value of the photo-electric current, expressed as the number of scale divisions that would be passed over in 100 seconds.*

Experiments made August 7, 1905, with well-polished Zinc Plate illuminated by Lamp. Nernst Lamp on 110 volt circuit.

t (mins.).	$K_1e^{-\lambda_1 t}$.	$K_2e^{-\lambda_2 t}$.	I (calc.).	I (obs.).
0	538	1153	1691	—
1	467	1144	1611	1611
3	352	1128	1480	1427
5	266	1111	1377	1349
7	200	1095	1295	1280
9	151	1079	1230	1217
11	114	1063	1177	1174
13	86	1048	1134	1134
15	65	1032	1097	1096
17	49	1017	1066	1085
19	37	1003	1040	1040
21	28	988	1016	998
23	21	973	994	988
25	15	959	974	969
27	12	946	958	941
29	9	931	940	933
31	7	917	924	915
33	5	904	909	907
35	4	890	894	891
37	3	878	881	891
39	2	865	867	853
41	2	852	854	845
43	1	839	840	845

t (mins.).	I (calc.).	I (obs.).	*t* (mins.).	I (calc.).	I (obs.).
45	827	824	73	673	665
47	815	824	75	663	665
49	804	811	77	654	647
51	792	804	79	644	639
53	780	767	81	635	623
55	769	779	83	625	608
57	758	755	85	616	617
59	747	750	87	607	602
61	736	750	89	598	594
63	725	739	91	590	591
65	714	717	93	581	587
67	704	717	95	573	570
69	694	697	97	564	554
71	683	683	99	556	554

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* The actual observation was the time taken to pass over 100 scale divisions. One division per second corresponded to $0{\cdot}48 \times 10^{-12}$ ampère.

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In the fourth column we have the calculated value of the current, the number being the sum of those in the two preceding columns. The first exponential term falls to half value in 4·9 minutes, the second in 94 minutes, the constants of change being $\lambda_1 = 0{\cdot}141$ and $\lambda_2 = 0{\cdot}00737$. The first term accordingly diminishes in value rapidly and becomes inappreciable after

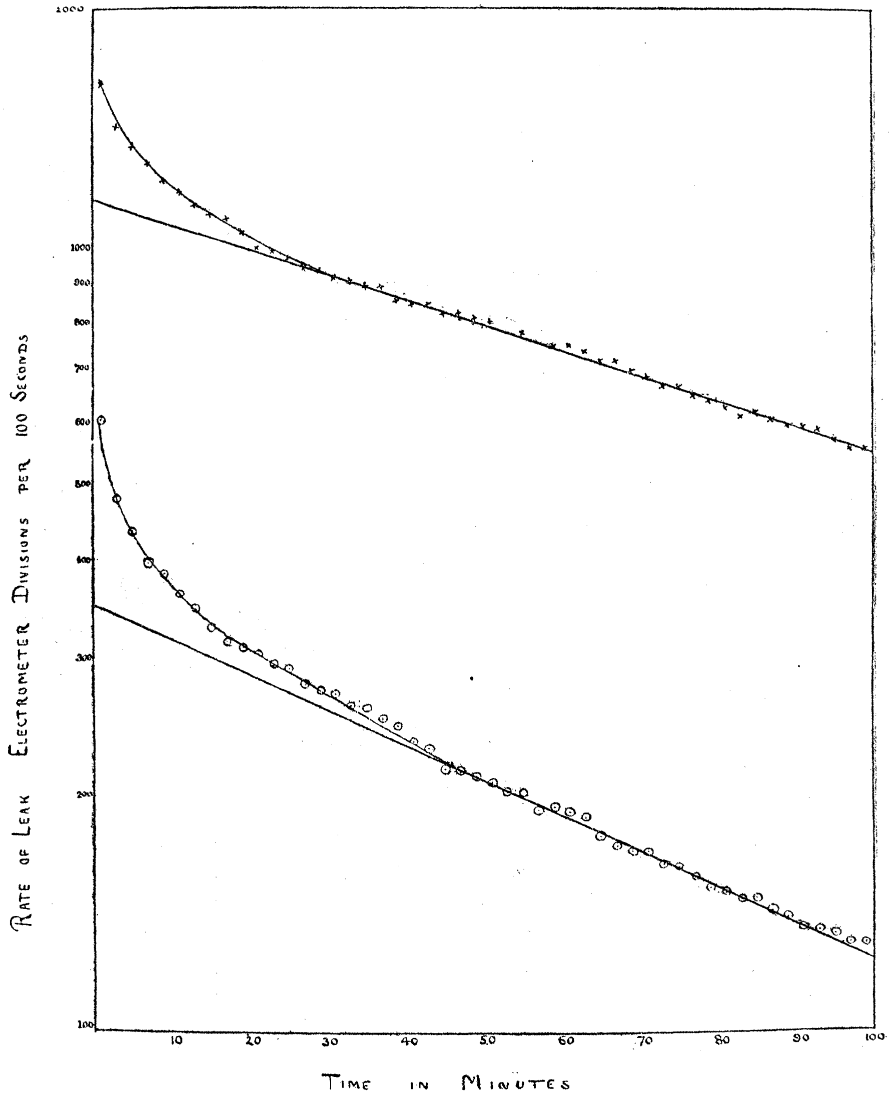

Fig. 3.

Photo-electric Fatigue of Zinc.

× Experiment made August 7, 1905, with well-polished zinc.

⊙ Experiment made July 24, 1905, with polished zinc. Nernst lamp taking 1 ampère on 110-volt circuit.

45 minutes. The values for the calculated current in the second part of the table are derived from the term $K_2e^{-\lambda_2 t}$.

6. These results are plotted on semi-logarithmic paper in fig. 3. On the same diagram is shown the fatigue curve for another experiment (July 24, 1905), in which the zinc plate was polished by hand instead of in the lathe, giving much smaller values for the photo-electric current. The constants of change in this case are $\lambda_1 = 0{\cdot}1365$ and $\lambda_2 = 0{\cdot}0104$, the time taken to fall to half value being 5 minutes and 67 minutes respectively.

7. The values found for λ_1 and λ_2 were of the same order as those just mentioned, in all the experiments carried out with polished zinc, although the conditions as to polish and to intensity of illumination were varied within wide limits. The rate at which the character of the surface changes under the influence of light is consequently not much affected by the conditions named.

8. *Results of Experiments with Amalgamated Zinc.*—Fatigue curves of a similar character were obtained with amalgamated zinc. One of the curves is shown in the lower half of fig. 4. In the rapid change at the outset the activity falls to half value in 4·2 minutes, the constant of change being $\lambda_1 = 0{\cdot}164$. The second change is much slower, the time taken for the activity to diminish one half being 167 minutes and the value of λ_2 being 0·00414. In this case K_1 is 854 and K_2 is 148 (scale divisions per 100 seconds), so that K_1 is about six times K_2.

9. The experiments I have carried out, using the Nernst lamp as a source of light, confirm in most particulars the results arrived at by Buisson* with sunlight. The chief point of difference is the clear recognition of the fact that the rate of decay at the outset is too great to be represented by the single exponential that is sufficient for the later stages. This is, in fact, mentioned by Buisson, but is attributed to experimental errors consequent upon the use of a gold-leaf electroscope. I have plotted some of his results, and find that they can be represented with far greater accuracy by employing two exponential terms.

10. *Theory of Successive Changes.*—The experiments already described show that the photo-electric activity of a zinc plate decays in a perfectly definite manner when a freshly-polished plate is exposed to light. The activity at any time t after the plate has been polished can be represented by an empirical formula containing the sum of two exponential terms,

$$I = K_1e^{-\lambda_1 t} + K_2e^{-\lambda_2 t}.$$

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* *Loc. cit.*

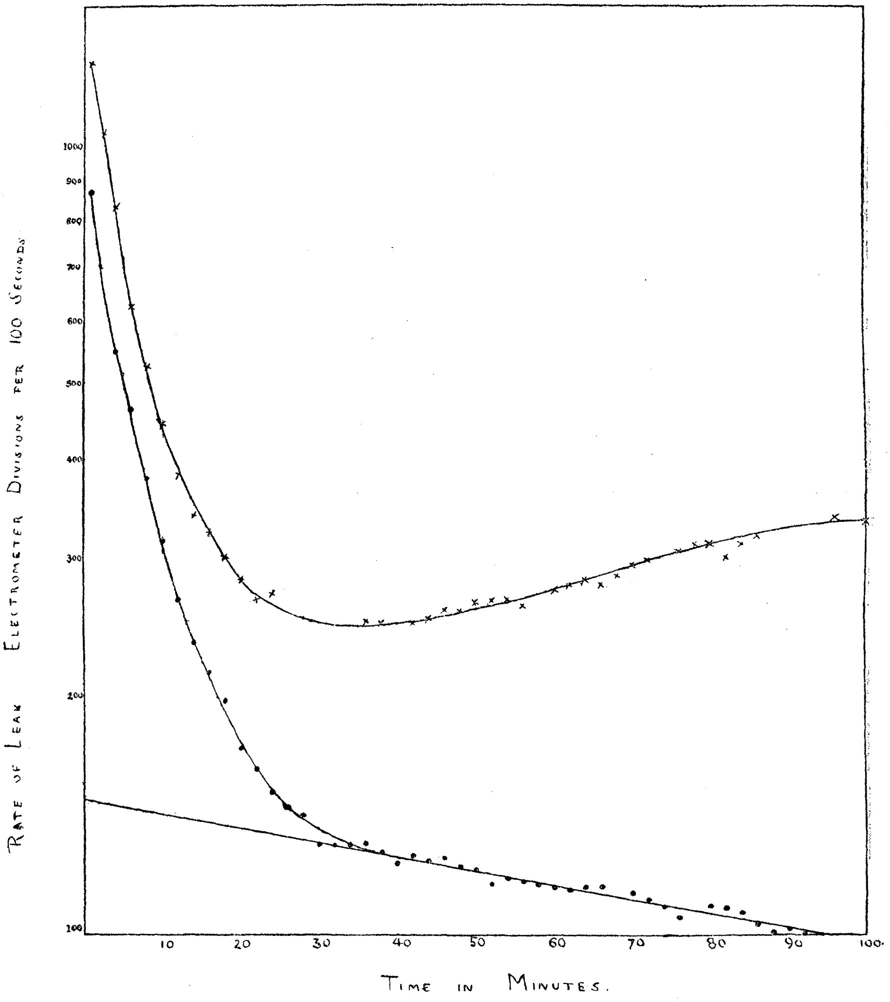

FIG. 4.

Photo-electric Fatigue of Amalgamated Zinc.

× Experiment made July 28, 1906, without absorbing solution.

● Experiment made August 1, 1906, with absorbing solution. Nernst lamp taking 1 ampère on 110-volt circuit.

To explain this result we assume that freshly-polished zinc (A) gives out negative ions under the influence of ultra-violet light, and changes to a form B (the change may be either a physical or a chemical one). B also gives rise to a supply of negative ions, and changes to a third form, C, which is supposed to be inactive.

At present we do not consider the nature of the substances (whether physical or chemical modifications of zinc) denoted by B and C.

Suppose we start with a quantity a of substance A. Let this change into B in such a way that the rate of change at any instant is proportional to the quantity still unchanged. Let B subsequently change into C, in accordance with the same law. If x, y, z denote the quantities of the several substances present at a time t,

$$x+y+z = a.$$

For the change from A to B

$$-\frac{dx}{dt} = \lambda_1 x, \quad \text{so} \quad x = ae^{-\lambda_1 t}.$$

The quantity λ_1 is the "velocity coefficient" of the first change.

The rate at which B accumulates is equal to the quantity supplied by A, less the quantity that changes into C, thus—

$$\frac{dy}{dt} = \lambda_1 x - \lambda_2 y,$$

λ_2 being the velocity coefficient for the second change.

This gives

$$\frac{dy}{dt} + \lambda_2 y = a\lambda_1 e^{-\lambda_1 t}.$$

To solve this equation we assume

$$y = \mathrm{D}e^{-\lambda_1 t} + \mathrm{E}e^{-\lambda_2 t}.$$

Substituting this value, we find

$$-\mathrm{D}\lambda_1 + \mathrm{D}\lambda_2 = a\lambda_1, \quad \text{or} \quad \mathrm{D} = -\frac{a\lambda_1}{\lambda_1-\lambda_2}.$$

When $t = 0$, $y = 0$; so $\mathrm{E} = -\mathrm{D}$, giving

$$y = \frac{a\lambda_1}{\lambda_1-\lambda_2}(e^{-\lambda_2 t} - e^{-\lambda_1 t}).$$

Thus, finally, we obtain as the values* of x, y, and z,

$$x = ae^{-\lambda_1 t},$$

$$y = \frac{a\lambda_1}{\lambda_1-\lambda_2}(e^{-\lambda_2 t} - e^{-\lambda_1 t}),$$

$$z = a\left(1 + \frac{\lambda_2}{\lambda_1-\lambda_2}e^{-\lambda_1 t} - \frac{\lambda_1}{\lambda_1-\lambda_2}e^{-\lambda_2 t}\right).$$

We assume that the observed photo-electrical activity is due in part to the substance A, in part to the substance B, so that we write

$$\frac{\mathrm{I}}{\mathrm{I}_0} = \frac{\mathrm{A}x+\mathrm{B}y}{\mathrm{A}a},$$

where A and B are constants measuring the activity of the corresponding substances.

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* These results are given in Rutherford's 'Radio-activity' (Second Edition, § 197).

Substituting for x and y we obtain

$$\frac{\mathrm{I}}{\mathrm{I}_0}=\left(1-\frac{\mathrm{B}}{\mathrm{A}}\,\frac{\lambda_1}{\lambda_1-\lambda_2}\right)e^{-\lambda_1 t}+\frac{\mathrm{B}}{\mathrm{A}}\,\frac{\lambda_1}{\lambda_1-\lambda_2}e^{-\lambda_1 t}.$$

This expression is of the required form, provided the coefficients are both positive quantities, for the empirical results can be represented by the sum of two exponential terms.

To satisfy this condition λ_1 must be greater than λ_2, *i.e.*, the first change must be the more rapid one.

In the experiments already described λ_1 was large in comparison with λ_2, so that an approximate value of the activity is given by

$$\frac{\mathrm{I}}{\mathrm{I}_0}=\left(1-\frac{\mathrm{B}}{\mathrm{A}}\right)e^{-\lambda_1 t}+\frac{\mathrm{B}}{\mathrm{A}}\,e^{-\lambda_2 t}.$$

As K_1 is of the same order of magnitude as K_2 for zinc, we should require to make A approximately twice as great as B.

11. *Recovery Due to the Longer Light Waves.*—In some of the experiments, more particularly with amalgamated zinc, the rapid fatigue at first observed was followed by a gradual recovery of the activity to a maximum value, which was, however, far smaller than the initial value. After this maximum value was passed the ordinary slow decay set in. This effect is illustrated in the upper curve of fig. 4, which shows the first part of the fatigue curve with the sudden fall in activity at the start followed by a gradual rise. The subsequent slow decay is not shown here.

The small recovery observed in these cases was traced to the action of the longer waves from the Nernst lamp. It was very much diminished by filling the cell in the cover of the testing vessel with water and was completely eliminated when the water was replaced by a solution of alum. The fatigue curve obtained with amalgamated zinc when the longer waves are absorbed is shown at the bottom of the same figure.

This action of the waves of greater wave length may be due simply to a temperature effect, for the photo-electric activity of metals is in general greater at a high temperature than at a low one; or it may be analogous to the effect observed by Buisson,* who found that all radiations do not work in the same sense as regards the contact difference of potential.

12. *Experiments on Zinc in a Vacuum.*—Ladenburg† has shown that many metals exhibit photo-electric fatigue in a vacuum. Buisson‡ also maintains that the alteration in a metallic surface produced by sunlight is independent of the pressure. On the other hand, Varley§ states that zinc illuminated by the light of an iron arc shows little or no sign of fatigue when the pressure

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* *Loc. cit.* † *Loc. cit.* ‡ *Loc. cit.*

§ 'Phil. Trans.,' pp. 439—458, 1903.

is below, say, the tenth of an atmosphere. Smolochowski, in some unpublished experiments on the liquid alloy of sodium and potassium, found that the decay phenomena do not take place in a high vacuum.

I have carried out some experiments on zinc in a good vacuum obtained by Dewar's method of absorbing the gas by charcoal cooled in liquid air, and found that the light of a Nernst lamp produced unmistakable fatigue. The results, however, were not sufficiently accurate to allow satisfactory fatigue curves to be drawn.

13. *Summary and Conclusion.*—The experiments described in this paper show that it is necessary to employ the sum of two exponential terms in order to obtain an adequate representation for the photo-electric fatigue curve of zinc. Just as Rutherford has explained the curves of decay for the excited activity of radium and thorium as a consequence of successive changes, so it is possible to explain the present results as due to two consecutive changes. The nature of the modifications thus suggested is left an open question.

It is also shown that the longer waves of light can bring about a change in the opposite sense, that is to say, they can produce a certain amount of recovery of photo-electric activity.

In conclusion, I must express my great indebtedness to Lord Blythswood, in whose laboratory at Renfrew some of these experiments were carried out, and also to Professor H. A. Wilson for advice and suggestions during the period of my work in the Wheatstone Laboratory of King's College, London.

[*Note added October* 9.—In a paper published in the 'Philosophical Magazine' for the present month (pp. 414—418), Sir Wm. Ramsay and Dr. Spencer discuss the "tiring" of metals when exposed to ultra-violet light. The curves they have obtained for magnesium, zinc and tin show a number of breaks, the number corresponding to the number of valencies of the metal. In the case of aluminium at least five or six breaks were observed. The fatigue curves that I have obtained for zinc illuminated by the light of a Nernst lamp do not show these breaks,* unless the point at which the first rapid change becomes insensible is regarded as a break in the curve.

If the results given above are interpreted in terms of the theory put forward by Sir Wm. Ramsay and Dr. Spencer, the modification that I have called zinc B would presumably correspond to zinc which has lost the first of the "metallic corpuscles."]

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* This may, perhaps, be due to the fact that the same zinc plate was used repeatedly, being repolished before an experiment. According to Sir William Ramsay and Dr. Spencer, the breaks in the curve are much less persistent in such a case.